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Kinetics of Solute-Solvent Interaction in Aqueous Solution of Butyl Carbitol by Ultrasonic Methods

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Ultrasonic absorptions in the frequency range 4.5—220 MHz and sound velocities at 2.5 MHz were measured at 25 °C with aqueous solutions of Butyl Carbitol (diethylene glycol monobutyl ether) over the concentration range 0.497—3.00 mol dm^{-3}. Only a single relaxational process was observed and attributed to a perturbation of the equilibrium $AB \underset{k_{21}}{\overset{k_{12}}{\longleftrightarrow}} A+B$, where A is Butyl Carbitol as the solute and B is water as the solvent participating in the reaction. A data analysis has led to the estimates $k_{12}=3.4\times10^7$ s^{-1}, $k_{21}=2.0\times10^8$ dm^3 mol^{-1} s^{-1}, the standard volume change of reaction $\Delta V^\circ=0.32$ cm^3 mol^{-1}, and the standard enthalpy change $\Delta H^\circ=5.4$ kJ mol^{-1}. The effect of the hydrophobicity of solute molecules on the water structure is discussed by comparing the present results with previous ones for other aqueous nonelectrolyte solutions.

In a series of ultrasonic studies of aqueous solutions of nonelectrolytes,$^{1-8)}$ we have found that different ultrasonic absorptions appear in the MHz frequency range depending upon the structure of solutes. They have been interpreted in terms of conventional relaxation theory. In order to analyze the relation between ultrasonic properties and structures of solute, a further accumulation of absorption results is desired for various nonelectrolytes over a wide frequency range and a concentration range. For this purpose, we have chosen Butyl Carbitol (diethylene glycol monobutyl ether) as a solute and have compared results obtained with those for other solutions. Another purpose of the present investigation is to elucidate why double relaxational processes have appeared in some solutions and a single process has in other solutions even when the structures of solutes are quite similar.

Experimental

Butyl Carbitol from Tokyo Kasei Co., Ltd. was distilled once under reduced pressure. No impurity was found by the gas-chromatographic method. Doubly distilled water was used as solvent. Concentrations of solutions were determined by weight.

Ultrasonic absorption coefficients were measured in the range 4.5—220 MHz by the pulse method.$^{9)}$ Sound velocity was measured with an interferometer at 2.5 MHz. The temperature for measurements was 25 °C with a fluctuation within ±0.005 °C. The density of each solution was measured with a pycnometer, about 4.4 cm^3 in volume at various temperatures in order to determine thermal expansion coefficients. All ultrasonic, kinetic, and thermodynamic parameters were calculated with a microcomputer.

A complete set of ultrasonic absorption coefficients and velocities at various concentrations are available from one of the authors (S.N.) on request.

Results

No frequency dependence of α/f^2 is found in liquid Butyl Carbitol as is seen from Fig. 1, where α is the ultrasonic absorption coefficient and f is the frequency. A relaxational absorption is found at the concentrations above 0.701 mol dm^{-3}. With increasing concentration, the relaxational amplitude increases rapidly till 1.20 mol dm^{-3} and then decreases monotonously. The sound velocity in the solutions shows a maximum at around 0.804 mol dm^{-3}. Representative ultrasonic absorption spectra are shown in Fig. 1. In general, the sound absorption associated with a single relaxational process can be described by the equation

$$\alpha/f^2 = A/[1+(f/f_r)^2] + B, \tag{1}$$

where f_r is the relaxation frequency, A the relaxational amplitude, and B the background absorption. The absorptions over the concentration range 0.701—3.001 mol dm^{-3} are characteristic of a typical single relaxation. These ultrasonic parameters were determined so as to give the best fit of the experimental data to Eq. 1 by the nonlinear least mean square method. They are listed in Table 1 along with the results of the sound velocity, density, and thermal expansion coefficient as a function of analytical concentration, C_c. The values of α/f^2 calculated with the parameter thus evaluated are shown by the solid lines in Fig. 1.

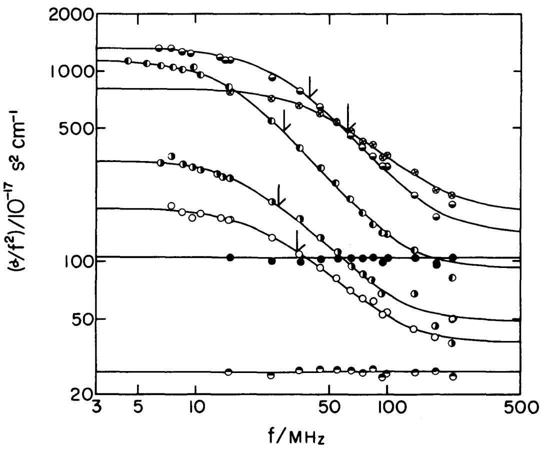

Fig. 1. Representative ultrasonic absorption spectra for aqueous solution of Butyl Carbitol at 25 °C. The arrows show the positions of the relaxation frequencies. The solid lines were calculated by means of Eq. (1). ◓: 0.497 mol dm^{-3}, ○: 0.750 mol dm^{-3}, ◑: 0.804 mol dm^{-3}, ◐: 0.990 mol dm^{-3}, ◒: 1.701 mol dm^{-3}, ⊗: 2.528 mol dm^{-3}, ●: pure Butyl Carbitol.

Table 1. Ultrasonic and thermodynamic parameters for aqueous solutions of butyl carbitol at 25 °C

C_e mol dm^{-3}	f_r[a)] MHz	A[a)] 10^{-17} s^2 cm^{-1}	B[a)] 10^{-17} s^2 cm^{-1}	ρ g cm^{-3}	c m s^{-1}	θ 10^{-4} deg^{-1}
0.701	47.0±0.9	77.9±0.8	30.0±2.0	0.9995	1568	3.9
0.726	46.5±0.9	99.4±1.1	29.0±2.5	0.9996	1568	3.5
0.750	33.9±0.7	151.2±1.1	38.0±1.7	0.9997	1569	3.8
0.804	27.2±1.2	293.3±3.1	47.6±3.1	0.9999	1572	4.1
0.900	26.7±0.8	604.6±3.7	57.7±2.2	0.9999	1572	4.1
0.990	21.7±1.1	1068±7	90.2±2.3	0.9999	1572	4.5
1.102	29.3±2.1	1152±24	79.4±5.7	1.0000	1568	4.6
1.200	30.1±2.1	1245±11	99.2±5.2	0.9997	1566	4.9
1.365	35.3±3.6	1252±25	110.9±9.6	0.9996	1562	5.1
1.701	39.1±4.6	1188±19	135.0±10.5	0.9982	1553	5.6
2.006	50.8±2.5	945.8±8.5	145.6±4.6	0.9971	1546	5.8
2.528	61.9±2.3	637.4±6.3	179.4±6.4	0.9950	1535	6.5
3.001	58.7±4.8	498.9±11.1	200.4±10.9	0.9915	1520	7.0

a) The errors in the ultrasonic parameters are the most probable ones.

As shown in Table 1, the relaxation frequency, which is related to the relaxation time τ, shows a curious concentration dependence, that is, the presence of a minimum. If the relaxation process results from usual reactions of the solutes, such a dependence may not be observed. The relaxational absorption seems to be a characteristic of the solution. Therefore, we consider a perturbation of equilibrium associated with the interaction between solute and solvent as the cause of the absorption. It is simply represented by the formula

$$\underset{C_1}{\mathrm{AB}} \underset{k_{21}}{\overset{k_{12}}{\longleftrightarrow}} \underset{C_2}{\mathrm{A}} + \underset{C_3}{\mathrm{B}}, \qquad (2)$$

where A is Butyl Carbitol, AB complex, and B water which interacts with the solute. The C_i's indicate the equilibrium concentrations of each component. In order to analyze the absorption mechanism, it is assumed that water consists of two states, *i.e.*, the hydrogen-bonded and nonhydrogen-bonded waters, and that the transition rates for these two states are too fast to be observed in our frequency range.[10)] It is also assumed that the nonhydrogen-bonded water may participate in the reaction. On these assumptions, the relation between relaxation frequency and analytical concentration is derived as,[3)]

$$1/\tau = 2\pi f_r = k_{21}[(C_e - \beta C_w + K_{12})^2 + 4\beta C_w K_{12}]^{1/2} \qquad (3)$$

where β is the molar fraction of the nonhydrogen-bonded water, C_w the analytical concentration of water, and K_{12} is defined as $K_{12} = k_{12}/k_{21}$. The rate and thermodynamic parameters, k_{21}, β, and K_{12}, are assumed to be independent of the concentration in the limited range studied. These parameters were determined so as to give the best fit of the observed relaxation frequencies to Eq. 3 as follows: The values of f_r obtained experimentally show a minimum at around 1 mol dm^{-3} and this result provides the relation between β and K_{12}.[3)] Initially, a value of β was assumed and K_{12} was calculated. Then, the rate constant k_{21} was determined so as to fit the experimental relaxation frequencies to Eq. 3 using the least mean square method. This procedure was repeated until the value of standard deviation (S.D.) reached a minimum. In this calculation, the smallest S.D. was obtained when C_e was 1.15 mol dm^{-3}. However, the result at 3.001 mol dm^{-3} was not used since it remarkably deviates from smoothed curve. The values of relaxation frequency calculated from the parameters evaluated are shown by the solid line in Fig. 2.

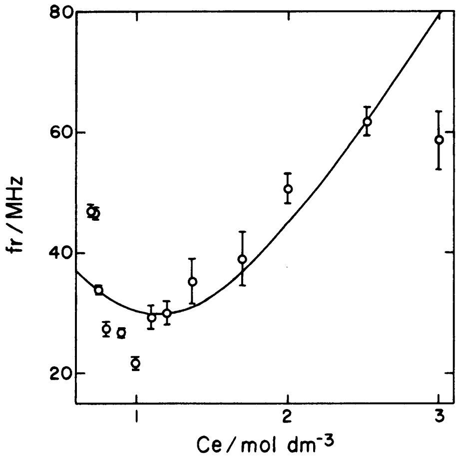

Fig. 2. Concentration dependence of the relaxation frequency for the aqueous solution of Butyl Carbitol at 25 °C. The solid line was calculated by means of Eq. (3) [S. D.=6.40 MHz].

Another parameter obtained from the measurements of the ultrasonic absorption and the velocity is a maximum excess absorption per wavelength, μ_m, which is expressed by the following equation on the assumption that the contribution of the relaxational specific heat is small:[3)]

$$\mu_m = Af_r c/2 = \pi \rho c^2 \Gamma(\Delta V^\circ - \theta \Delta H^\circ/\rho C_p)^2/2RT \qquad (4)$$

where ρ is the density of solution, R the gas constant, T the absolute temperature, θ the thermal expansion coefficient, C_p the specific heat at constant pressure, ΔV° the standard volume change of the reaction, and

Table 2. COMPARISON OF THE RATE AND THERMODYNAMIC CONSTANTS FOR AQUEOUS SOLUTIONS OF SOME ETHERS AT 25 °C

Solute	$\frac{k_{12}}{10^7\ \mathrm{s}^{-1}}$	$\frac{k_{21}}{10^8\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}}$	$\frac{\Delta H^\circ}{\mathrm{kJ\ mol}^{-1}}$	$\frac{\Delta V^\circ}{\mathrm{cm}^3\ \mathrm{mol}^{-1}}$	β	Ref.
Allyl Cellosolve	3.0±0.2	3.7±0.2	8.0±3.0	0.60±0.35	0.121	7
Propyl Cellosolve	9.6±1.3	1.3±0.2	5.4±2.5	0.30±0.15	0.100	4, 8
Isobutyl Cellosolve	5.5±0.7	2.5±0.3	8.8±0.4	0.38±0.03	0.0428	4
Butyl Cellosolve	4.2±0.7	1.7±0.3	13.0±0.4	0.67±0.06	0.0290	2, 4
Butyl Carbitol	3.4±0.6	2.0±0.4	5.4±0.1	0.32±0.01	0.0277	This work

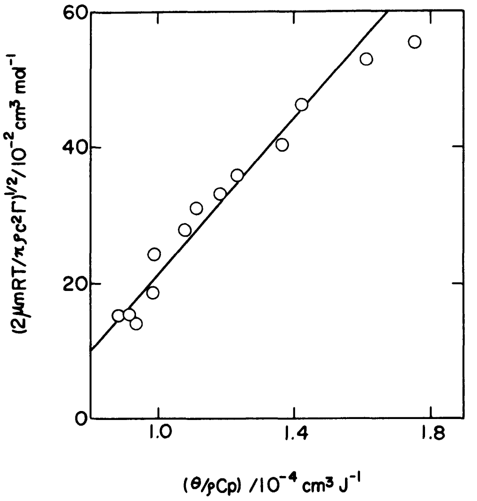

Fig. 3. The plots of $(2\mu_m RT/\pi\rho c^2\Gamma)^{1/2}$ vs. $\theta/\rho C_p$ for the aqueous solution of Butyl Carbitol.

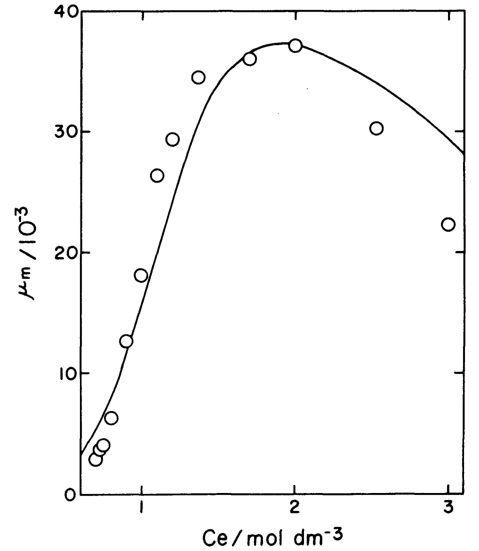

Fig. 4. Concentration dependence of the maximum excess absorption per wave length for the aqueous solution of Butyl Carbitol [S. D. $=3.75\times10^{-3}$].

ΔH° the standard enthalpy change. The term Γ is derived for the reaction under consideration as $[1/C_1+1/C_2+1/C_3-1/(C_1+C_2+C_3)]^{-1}$. As reported in previous papers,[1,2] the concentration dependence of μ_m is controlled mainly by the term $\rho c^2\Gamma$. Precisely, however, term $\theta/\rho C_p$ depends on concentration. Therefore, we assume that the specific heat is given roughly by $C_p=2.28n_e+4.18(1-n_e)$(J deg^{-1} g^{-1}) in obtaining values of ΔV° and ΔH°. Here, n_e is the molar fraction of Butyl Carbitol in the aqueous solution. The slope and intercept of $(2\mu_m RT/\pi\rho c^2\Gamma)^{1/2}$ vs. $\theta/\rho C_p$ plots shown in Fig. 3 provide with these values, as listed in Table 2. The concentration dependence of the density is well described by a cubic function of the analytical concentration of Butyl Carbitol as $\rho=0.99698+6.02505\times10^{-3}C_e-3.6627\times10^{-3}C_e^2+3.3096\times10^{-4}C_e^3$ (g cm^{-3}) [S. D.$=2.5\times10^{-4}$ (g cm^{-3})]; the sound velocity and thermal expansion coefficient are well expressed by the following polynomial equations: $c=1496.6+198.93C_e-179.32C_e^2+61.211C_e^3-7.5477C_e^4$ (m s^{-1}) [S.D.$=2.3$ (m s^{-1})] and $\theta=2.5295\times10^{-4}+2.1025\times10^{-4}C_e-2.0615\times10^{-5}C_e^2$ (deg^{-1}) [S.D.$=1.1\times10^{-5}$ (deg^{-1})]. The solid curve in Fig. 4 shows the values of μ_m which were calculated with the above thermodynamic parameters and Eq. 4.

Discussion

In order to interpret the observed relaxational process, several kinetical conditions have been applied: Firstly, even if the condition of water molecule is altered by addition of a solute, the association and dissociation processes between water molecules are too fast to be observed since their rates are estimated to be of the order of 10^{-12} s.[10] Secondly, any relaxation due to the internal rotation of solute may be ruled out because the concentration dependence of the observed relaxation frequency cannot be explained in terms of such a unimolecular reaction, and actually no relaxation phenomenon is found in pure Butyl Carbitol. Thirdly, the relaxation process due to the hydrogen bonding association of Butyl Carbitol molecules is probable. However, such a relaxation process is expected to be far beyond the MHz frequency range on the basis of estimates for various alcohols.[11,12] The high values of the background absorptions suggest the existence of such processes. Fourthly, although the association process of Butyl Carbitol molecules due to hydrophobic interaction is also conceivable, such phenomenon has been found for other ethers[1-4] with larger hydrophobic groups in lower frequency range than the observed frequency range. Finally, there is left only the relaxation process due to an interaction between ether and water molecules associated with hydrogen bonding, which has been shown to be capable of good interpretation of the experimental results in the preceding sec-

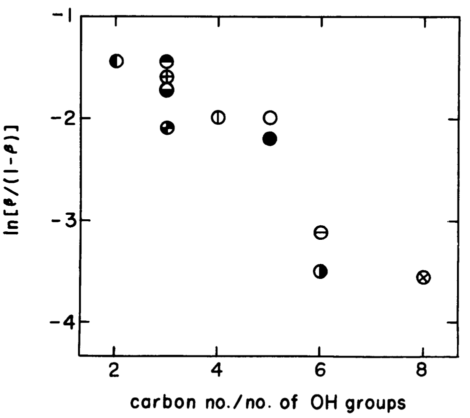

Fig. 5. Plots of the values of $\ln[\beta/(1-\beta)]$ *vs.* the carbon number per hydroxyl group for the aqueous solutions of a series of alcohols and ethers. ◐: 1,2-Butanediol, ◓: Allyl alcohol, ⊕: Isopropyl alcohol, ◒: Propyl alcohol, ◕: 1,6-Hexanediol, ⦶: *t*-Butyl alcohol, ○: Allyl Cellosolve, ●: Propyl Cellosolve, ⊖: Isobutyl Cellosolve, ◑: Butyl Cellosolve, ⊗: Butyl Carbitol.

tion. According to our model, it is possible to estimate qualitatively the effect of Butyl Carbitol molecule on the water structure. The molar fraction β of nonhydrogen-bonded water in the aqueous solution which is calculated from Eq. 3 is listed in Table 2 along with those previously reported. The values may be taken to correspond exactly to the fraction of water capable of interacting with the solute or that of the less structured water molecules. The value for pure water is not less than 0.24.[13] On the other hand, those in the aqueous solutions are smaller than that of the water. This means that the addition of such nonelectrolytes into water causes water molecules to enter a more stabler state. This seems to be due to the hydrophobicity of the solute molecule. In order to examine its effect on the water structure we have plotted $\ln[\beta/(1-\beta)]$, which is related to the free energy change between the two states of water, against the carbon number per hydroxyl group for a series of alcohols and ethers, obtaining Fig. 5. With increasing carbon number per hydroxyl group, the value of $\ln[\beta/(1-\beta)]$ decreases, that is, the absolute value of the free energy change increases. This plot indicates that the ability to promote the water structure will increase with increasing hydrophobicity of the solute molecule.

It is interesting to note that a single relaxation process has been observed in the aqueous solution of Butyl Carbitol, whereas double relaxations are found in a solution of Butyl Cellosolve.[2] In the latter solution, one process is the same as that observed for Butyl Carbitol solution and the other, found around 7 MHz, has been attributed to a perturbation of equilibrium associated with an aggregation due to the hydrophobic interaction. The difference between the ultrasonic properties of these solutions may arise from the size of oxyethylene group, and the electrorepulsive force may affect the formation of the aggregate. This kind of difference has also been found in aqueous solutions of propyl alcohol[3] and Propyl Cellosolve.[8]

There is another interpretation for the absorption phenomenon in aqueous solutions of nonelectrolytes, which is based on the fluctuation model. Atkinson *et al.*[14–16] successfully analyzed observed absorptions in dioxiane, butylamine, and tetrahydrofuran solutions, which gave broad absorption spectra. They questioned the validity of such an approach as adopted in this report for reasons of unreliable complex formation, too slow rates for the hydrogen bonding, and inconsistent thermodynamic constants. However, as for the aqueous solution of Butyl Carbitol, a clear single relaxational absorption is observed, the simple 1-1 complex exists with equilibrium between the nonhydrogen-bonded water and single solute, the rate constant obtained corresponds to the overall process for the interaction in which the diffusion and rotation of reactants are also included, and the enthalpy change for the reaction seems reasonable because one reaction site is surrounded by many polar molecules.[17]

In conclusion, it has been elucidated from the present ultrasonic experiments for a series of alcohol and ether solutions that the ultrasonic absorption character will depend on the structure of solutes, that is, a single relaxational process occurs in solutions in which solutes have a relatively small hydrophobicity, whereas double relaxations appear with increasing hydrophobicity of solutes.

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